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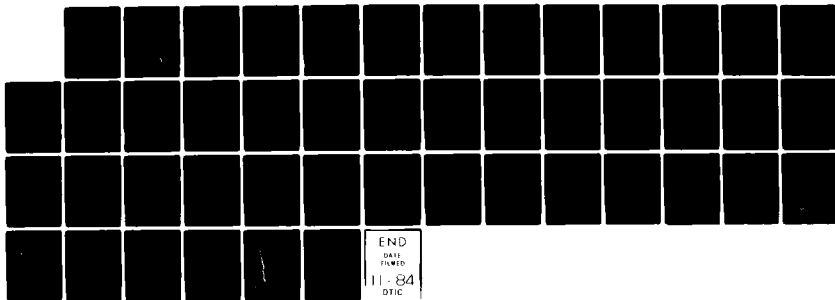
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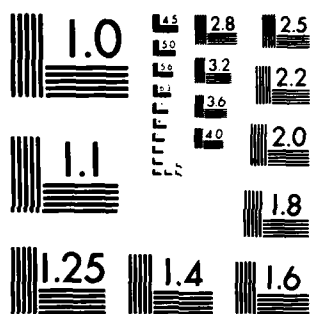
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STORAGE STABILITY OF JET FUELS

Final Report

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Catholic University
of America

Washington, D.C. 20064

August, 1984

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This Final Report on Storage Stability of Jet Fuels covers the period Feb. 1983 to Aug. 1984. Persons participating in the research program during various times within this period are: Dr. N.F. Yaggi, Dr. M. Constance Loeffler, Ms. Junli Li, John Ge, and Sheng Lee.

The following five papers have been published or accepted:

1. Stabilities of Fuels Derived from Coal, Oil Shale, and Petroleum, N.C. Li, R.N. Hazlett, L. Jones, J. Ge, N.F. Yaggi, C.M. White, Proc. Conf. on Long Term Storage Stabilities of Liquid Fuels, Israel, July, 1983.
2. Oxygen Absorption and Light Scattering Studies of the Stability of Liquid Fuels, N.F. Yaggi, S.H. Lee, J. Ge and N.C. Li, Preprints, ACS Div. Fuel Chem., 29 (1) 178 (1984), April, St. Louis, Mo.
3. Light Scattering, Oxygen Uptake and Deposit Formation in Studies of Stability of Coal-Derived and Petroleum Fuels, S.H. Lee, J.H.S. Ge and N.C. Li, Preprints, ACS Div. Petroleum Chem., August, 1984, Philadelphia, PA.
4. Storage Stability Studies of Fuels Derived from Shale and Petroleum, L. Jones, R.N. Hazlett, N.C. Li, J. Ge, Fuel, in press.
5. Light Scattering Studies of the Stability of Liquid Fuels, N.C. Li, R.N. Hazlett, J. Ge and N.F. Yaggi, Fuel, in press.

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Abstract:

Storage stabilities of jet fuels derived from petroleum were determined using laser light scattering, sediment formation, and oxygen uptake measurements. Fuel degradation was monitored in the presence of the following added specific compounds: 2,5-dimethylpyrrole (DMP), N-methyl pyrrole (NMP), thiophenol, thiophene, decanethiol, dibutyl sulfide, dibutyl disulfide, tetrahydrothiophene, hexadienes, 1-hexene, indene, and dimethyl quinoline (DMQ) and mixtures of these at various temperatures. The light scattering results are correlated with extent of deposit formation, which is an accepted measure of stability, and with oxygen uptake results. Light scattering intensity, weight of deposit (in mg/100 ml of fuel), and oxygen uptake increase with increase in storage time, concentration of added specific compound, and stress temperature. Temperature variations of these measurements give activation energies of the degradation reactions. We have obtained the first direct evidence of the pyrrole radicals in DMP and NMP when a fuel is degraded in the presence of the pyrrole. These two pyrrole radicals give widely different electron paramagnetic resonance parameters: g and line width values. Degradation products obtained by heat stressing (at 80-120° C) of fuels enriched with specific heteroatomic compounds were analyzed by nuclear magnetic resonance, electron paramagnetic resonance, infrared, X-ray photoelectron spectroscopy, and low voltage high resolution mass spectrometry. In the DMP sediment, oxygen is incorporated as carboxylate and carbonyl groups. However, in the presence of thiophene and DMP, NMR spectra show presence of appreciable methyl and aromatic or olefinic carbons (pyrrole) and very small amount of carbonyl and carboxylate.

INTRODUCTION

Jet fuels may be considered as hydrocarbon fuels because the heteroatom (O,N,S) contents amount to only a few tenths of one percent. However, these trace impurities exert significant deleterious effects on the stability of the liquid fuels by promotion of deposit formation upon storage, and the problem is becoming worse because of increased use of lower grade petroleum crudes. We have studied the effects of trace impurities on the stability of liquid fuels, in order to understand the mechanisms of deposit formation on aging of hydrocarbon fuels.

The objective of the research was to determine the effect of fuel composition on storage stability of broad range jet fuels and define the role of added material on formation of solids. The fuel was degraded by addition of nitrogen, sulfur, and unsaturated compounds, and mixtures of these. The interactions involving the added material and the fuel were defined.

Light scattering technique was used extensively to examine the growth of small particles, which are precursors to deposit formation. As a fuel ages, particles grow in size and scatter

light, so that light scattering measurement has greater sensitivity for initial deposit formation and could speed up the determination of fuel stability. This is especially important since deposit techniques for determining the stability of liquid fuels require weeks or months of storage even at elevated temperatures. However, the relationship between particle formation and growth as determined by light scattering and standard stability tests has not been fully established. Thus quantitative measurements on sediment formation by traditional accelerated tests constituted a parallel part of this study. When we understand the mechanisms of deposit formation and the nature of the deposit, ways can be found to retard its formation.

EXPERIMENTAL

Previous work (1,2) has developed promising information on the relationship of light scattering to fuel stability. We have tested effects of added materials, such as nitrogen, sulfur and unsaturated compounds present in petroleum, on extent of solid formation and extent of light scattering in the fuel.

Laser light scattering measurements were carried out using a photometer described by Berry⁽³⁾ modified by introduction of

a laser light source (Spectra-Physics Model 155 0.5 mW He-Ne laser, 632.8 nm). Light scattering cells of design by Dandliker and Kraut⁽⁴⁾ were used. The cells were made of thin-walled borosilicate glass and were in the form of truncated cones, in order to reduce the stray light pickup by the detector. The volume capacity of the cell was approximately 10 mL; in most cases a 7 mL sample volume was used.

Light scattering intensities are reproducible to ± 0.02 , when the change in intensity is regular and small. However, when the scattering intensity is changing very rapidly, as in the inflection region of Fig. 1, the reproducibility becomes poorer. When larger particles form and settle, no further scattering data are recorded.

The light scattering cell is only partially filled with liquid. The air space above the liquid supplies all the oxygen necessary during the light scattering experiment. The fuel storage tests, both gravimetric determination of sediments and light scattering measurements, are conducted in the presence of air.

The additives were weighed in volumetric flasks and then filled to the mark with liquid fuel; the time of mixing was

taken as zero time. The liquid was then introduced into a light scattering cell; the cell was mounted in a cell holder, which in turn was mounted in the cell compartment. Care was taken to insure proper alignment of the cell with the very narrow light beam and the detector. The instrument was calibrated periodically by replacing the cell with a turbid standard glass block.

In order to determine the extent of sediment formation and to obtain a sufficient amount of sediment for its characterization, we carried out accelerated storage stability tests by adding 200 mL of a liquid fuel containing an additive to a Pyrex Erlenmeyer flask. Stoppered samples were stored in darkness at various temperatures for various time intervals. After storage, flask contents were filtered through a Buchner funnel equipped with a weighed filter paper that had been dried in an oven at 110 C° for 1.5 hours.. The flask and Buchner funnel filter were washed with n-heptane, dried in a vacuum oven at 110° for 1.5 hrs and allowed to cool under vacuum. The insoluble sediment and adherent sediment were determined gravimetrically and summed to give total deposit weight, as described by Brinkman, Hazlett, et al. (5,6)

Electron paramagnetic resonance (EPR) experiments were carried out in the laboratory of Dr. D.W. Pratt at the University of Pittsburgh, using a Varian E-4 EPR spectrometer. The scan time was 8 min., with a filter time constant of 0.30 s. The field was modulated at a frequency of 100 kHz and an amplitude of 2 gauss/. The microwave frequency was 9.08 GHz with the microwave power of 1.98 mW.

High resolution mass spectrometric investigation of a deposit was performed by Dr. Curt White at the Pittsburgh Energy Technology Center, using a Kratos MS-50 ultra-high resolution mass spectrometer equipped with a DS-55 computer for data storage and reduction. The solid (30 μ g) was introduced into the mass spectrometer source via a direct insertion probe at 573 K. The instrument was operated at 25000 dynamic resolution, 11.5 V ionization potential, and a scan speed of 1000 s per decade. A mixture of halogenated aromatics was used as the mass standard.

X-ray photoelectron spectroscopy (XPS) spectra of the insoluble sediments were obtained at the University of Pittsburgh with a Leybold Heraeus LHS-10 Surface Analysis System. The spectrometer is interfaced to a HP 1000 computer used for spectral accumulation and data processing. Non-monochromatized Al K_α radiation (1486.6 eV) was used. All binding energies were referenced to the C 1s line (285.0 eV)

Cross polarization/magic-angle spinning (CP/MAS with C-13) NMR experiments were carried out at Colorado State University Regional NMR Center, using NT-150 wide-bore Nicolet Fourier-transform NMR spectrometer, and at the University of Utah on a Bruker CXP-100 instrument. At Utah several dipolar dephasing experiments, involving a 40 μ sec. delay inserted between the contact time and the acquisition period, were carried out.

Samples of petroleum jet fuel, A (LR 31613#3) and 80-8, were obtained from Dr. D.C. Cronauer, Gulf Research and Development Co. and Dr. R.N. Hazlett, Naval Research Laboratory.

The latter sample from a Gulf coast refinery was colorless. Petroleum JP-5 (80-12) from a West coast refinery was yellow. Dr. Cronauer also kindly furnished the following petroleum fuels: jet fuel (LR-31284), and diesel fuel (LR30886). Table 1 lists some properties of the last two fuels and JP-5 (80-12). No specification data on other samples are available.

RESULTS

(a) Deposit Formation

Table 2 lists the insoluble sediment, adherent sediment, and total sediment, W, formed when 200 mL jet fuel A (LR31613#3) containing added 0.0286 M DMP was stressed at 43°, 67°, 80°, for various time intervals. Figure 2 gives plot of W vs. time for each of the three temperatures. For each stress period (2,4,6,8, 10 or 12 days), a plot of $\ln W$ vs. $1/T$ is linear as shown in Figure 3.

Table 2 gives also sedimentation results for blanks (no DMP added to the fuel) after storage for 12 days. If the total sediment from a 0.0286 M DMP solution in jet A, corrected for blanks, is proportional to specific rate constant for the degradation of the fuel, then the temperature variation data can be used to calculate the apparent activation energy. The linear Arrhenius plot yields $E_a = 12.7$ kcal/mole, the same as that reported by Frankenfeld et al.⁽⁵⁾ for a 0.107 M DMP solution in a petroleum-derived jet fuel from the Bayway, NJ, refinery. The result of Frankenfeld et al. was for 14 days storage in the temperature range 23-68° C, whereas our result was for 12 days storage in the temperature range 43-80°C.

Comparison of Tables 2 and 3 shows that DMP promotes sedimentation formation much more strongly than does NMP. Of the sulfur-containing compounds, the ability to promote sediment formation varies in the order: thiophenol > thiophene, tetrahydrothiophene > dibutyl disulfide, dibutyl sulfide, decanethiol. Indene is slightly more deleterious than the aliphatic thiol, decanethiol. The presence of 0.2M 1-hexene or 0.2M 1,5-hexadiene with 0.0286M DMP gives the same amount of sediment as 0.0286M DMP (0.0159 g/100 mL fuel). The presence of thiophenol with 0.0286 M DMP, however, gives much more sediment than expected (positive synergism)

From the temperature variation of total sediment weights, corrected for blanks, the apparent activation energy for the degradation of the jet fuel A in the presence of 0.1 thiophenol, 4 days, is $E_a = 11.0$ kcal/mole. This is to be compared with $E_a = 12.7$ kcal/mole for degradation of the same fuel in the presence of 0.0286M DMP, 12 days.

Table 4 lists sedimentation results for petroleum jet fuel (LR29792), JP-5 (80-8, 8-12) and diesel fuel. The effects of dopants on two different specification grade petroleum JP-5's is noteworthy. Table 4 shows that JP-5 (80-12) gives rise to much more sediment formation and greater positive synergism between DMP and thiophenol than does JP-5 (80-8). For petroleum JP-5 (80-8), the effect of DMP and thiophenol is additive. Synergism between these additives occurs most dramatically with petroleum-derived diesel fuel. Table 1 shows that among the fuels tested, the petroleum-derived diesel fuel contains the lowest amount of saturates and the largest amount of aromatics and sulfur. White (7) reported that for petroleum products, hydrocarbon composition influences stability, and the stability decreased in the order: paraffins, naphthenes, aromatics, olefins and diolefins. In general this is the order of susceptibility to antioxidative attack and polymerization reactions which are important causes of sediment formation.

Table 5 gives results of duplicate determination of sediment formation when jet fuel (LR-31284) is stressed at 50°C for 14 days in the presence of 2,6-dimethylquinoline (DMQ), and 0.1 M sulfur-containing or 0.1M unsaturated compounds. The ability to promote sediment formation decreases in the order: thiophenol, 1,5-hexadiene, dibutyldisulfide, 1-hexene, dibutyl sulfide, and tetrahydrothiophene. In the presence of DMQ and thiophenol, again there is a positive synergism, similar to that for DMP-thiophenol.

(b) Light Scattering

Figure 1 shows that in the absence of additive, petroleum jet fuel, shale-derived jet fuel (JP-5) and the most severely hydrotreated H-coal (LHSV 0.5) (8) exhibit no increase in light scattering at 90° scattering angle, I_{90} , over a period of 160 hrs. On the addition of approximately 200 ppm (N) as 2,5-dimethylpyrrole (DMP), the intensity curves for the three fuels are *very similar*.

to each other. For mixtures of H-coal liquid (LHSV 0.5) and petroleum JP-5, after storage at room temperature for 20 h, a plot of I_{90} vs. volume fraction of H-coal liquid in the binary mixture, from 0 to 1.0 is linear. This observation is important and indicates that the mixtures of these fuels exhibit ideal behavior, i.e., no apparent molecular interaction has occurred. In a time of dwindling petroleum supply, it is important to know that blends of some petroleum products and some upgraded coal-derived liquids are compatible, and may be blended without loss of stability.

Figure 4 shows plots of light scattering intensity at 90° scattering angle for petroleum JP-5 (80-12) containing 50 ppm (N) DMP and various additives. The presence of 0.2M thiophene, 0.2 M 1,5-hexadiene, or 0.2M thiophenol alone in the petroleum JP-5 results in no change in I_{90} . In the presence of DMP however, thiophenol gives the largest light scattering followed by hexadiene and then thiophene. The implication is that these individual sulfur-containing compounds by themselves are not deleterious to the stability of the liquid fuel. However, in the presence of nitrogen-containing compound like DMP, the instability effect is shown. Therefore, the combined effect of nitrogen and sulfur-containing compounds must be considered. The order of instability is thiophenol > 1, 5-hexadiene > thiophene.

Figure 5 shows plots of I_{90} for petroleum jet fuel A containing 0.2 M indene and 0.2 M decane thiol at 25° and 80° . At a given temperature, indene promotes greater instability than decanethiol. As temperature increases, the extent and rate of degradation, as evidenced by increase in light scattering, also become larger. Figure 2 shows that deposit formation increases with higher temperature, so that sedimentation and light scattering are parallel measures of instability.

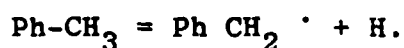
Figure 6 shows that dibutyl disulfide promotes greater light scattering for petroleum jet fuel A than dibutyl sulfide. We have already provided sedimentation data, Table 3, to show that the ability to promote sedimentation is also greater for the disulfide than for the monosulfide. The greater ability of the disulfide, as compared to the monosulfide, may be due to the greater tendency of the disulfide to form thiyl (R S.) radical

(c) Oxygen Absorption Measurements

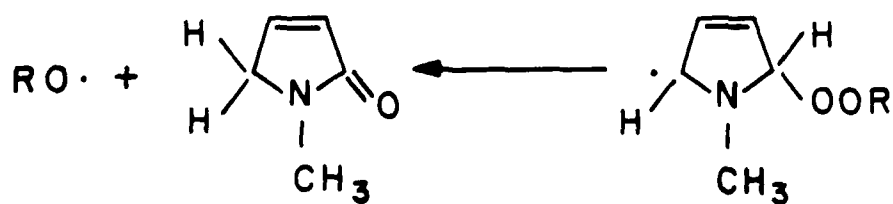
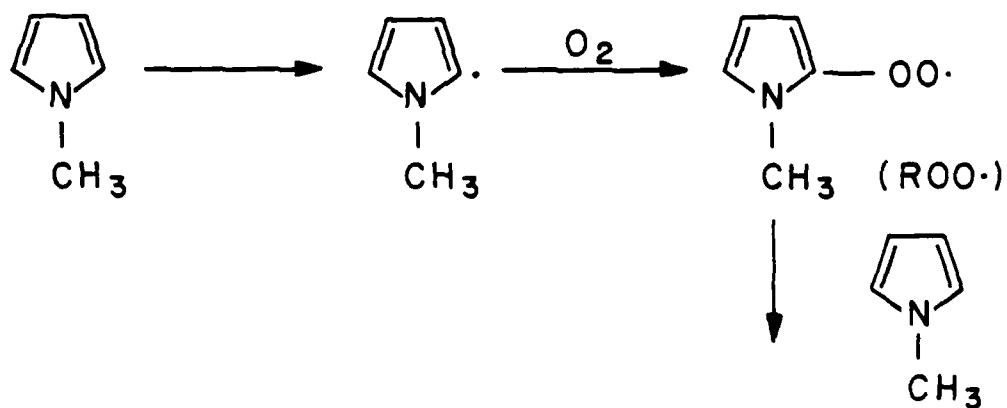
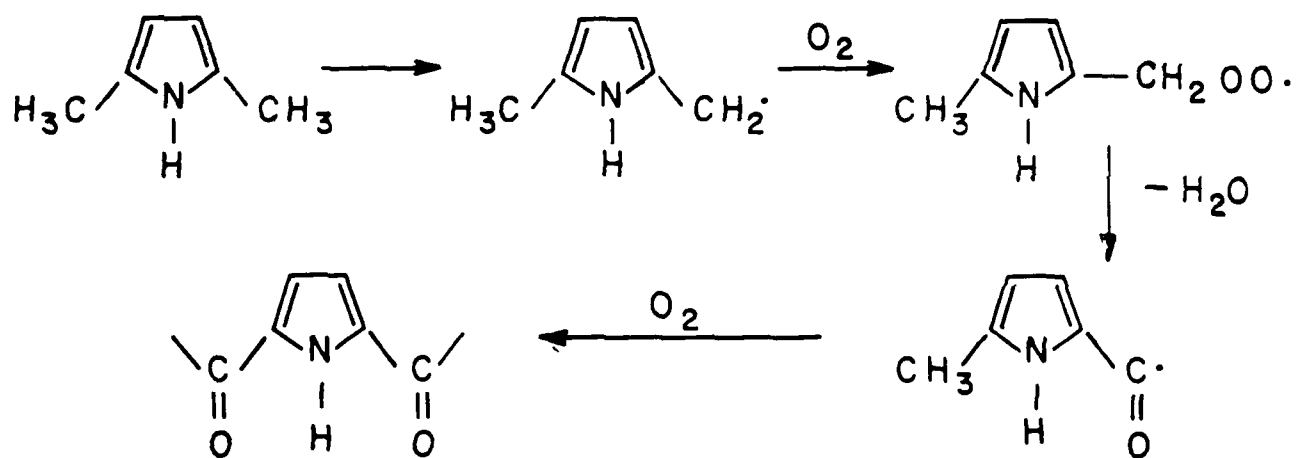
Oxygen absorption measurements were carried out in the manner described previously (9). Figure 7 gives plots of moles O_2 absorbed per mole of N-methyl pyrrole (NMP) vs. time at three temperatures. Increase in temperature means increase in accelerated ageing and therefore results in greater oxygen uptake. At a given temperature, longer storage time results in more ageing and greater oxygen uptake. Jones, Hardy, and Hazlett (10) have shown that for petroleum-derived diesel fuel marine, increase in stress temperature results in a shorter time necessary to form equivalent weights of total insolubles. The data of Fig. 7 also show that increase in temperature results in a shorter time necessary to absorb equivalent amount of oxygen per mole of NMP. A plot of $\log t$ vs. $1/T$ can be constructed, where t is time in hours required at any particular temperature of stressing to absorb 0.01 mole O_2 /mole NMP. The plot is almost linear. Figure 7 also shows that 2,5-dimethylpyrrole (DMP) exhibits much higher oxygen

uptake than does NMP. This correlates with the fact that DMP promotes very drastically the formation of insoluble gums and light scattering in fuels, whereas the effect of NMP is much smaller. Reactions leading to sediment formation in the presence of pyrroles may be characterized as free radical, autoxidative reactions, and parts of the proposed reaction sequences are given in Scheme 1 (5,11).

The formation of the DMP radical (I) from DMP may occur more extensively than the formation of NMP radical (III) from NMP, if one considers the following analogy: the heats of formation (ΔH_f (g) at 298 K) of the benzyl radical ($\text{PhCH}_2\bullet$) and phenyl radical (Ph \bullet) are 42 and 80 kcal/mole, respectively (12). Also, the heats of radical formation for the reactions



are 85 and 112 kcal/mole, respectively. The extent of radical formation may explain the greater and faster oxygen uptake by DMP than NMP and the fact that DMP promotes sediment formation in fuels much more strongly than does NMP. Additionally, in Scheme 1, for NMP in going from IV to V, a hydrogen transfer is involved. If this is a rate determining step, then the slower oxygen uptake by DMP can also be explained. The possible formation of $\text{N-CH}_2\bullet$ radical for NMP is not included in Scheme 1, because the N-CH_3 group remains intact during autoxidation (11).



However, since Smith and Jensen (11) could account for only 30% of oxygen absorbed, the overall oxidation of NMP probably involved several parallel reactions not shown in Scheme 1.

Figure 8 shows that the oxygen uptake by 2,4-hexadiene is greater than 1-hexene. This is in line with the greater effect on instability of fuel caused by a diolefin as compared with a monoolefin (7)

(d) EPR measurements

We have obtained the first direct evidence (from EPR) of the pyrrole radicals in DMP and NMP. Fig. 9 gives EPR spectrum of a deposit formed from stressing jet fuel A with 0.0286 M DMP at 80°, 6 days. The spectrum gives $g=2.0041$ and the line width, $\Delta H_{pp} = 10.8$ gauss. Similar EPR spectra are obtained from deposits isolated from the same solution when stressed at 80° C for 2,4,8, 10 and 12 days. With NMP, a 10-fold increase in concentration is necessary to produce sediment in the jet fuel A when stressed at 80° C for the same period of time. The EPR spectrum of a sediment formed from stressing the same jet fuel with 0.286 M NMP at 80° C, 6 days, gives $g=2.0017$ and $\Delta H_{pp} = 5.4$ gauss. The lower g and line width of the NMP radical, compared to the DMP radical, are significant and merit further experimentation with EPR spectroscopy.

(e) Characterization of deposits

A sediment (yield=3.5 mg/mL of fuel) was obtained by stressing petroleum JP-5 (80-8) with 0.0286M DMP at 120° C, 10 days. The magic angle, solid-state C-13 NMR spectrum of the sediment is shown in Fig. 10 (top), while the bottom spectrum was obtained on the same deposit using a dipolar dephasing pole sequence in which 40 μ sec post delay has been inserted. In work on highly crystalline material, Pugmire et al⁽¹³⁾ have shown that protonated carbons would be broadened out into the base line and not observable at 40 μ sec. In our sample, the broadening of the aliphatic group signals does not occur. This indicates that there is a relatively high degree of mobility in the aliphatic groups.

The aromaticity of the sediment is 0.70, while DMP and the fuel have aromaticities of 0.66 and 0.10, respectively. These data support the suggestion that DMP products are a part of the deposit. The spectra shown in Fig. 10 indicate the presence of variable functions including aliphatic CH_3 and CH_2 (20-24 ppm), aromatic (or olefinic pyrrole) carbon (110-150 ppm), as well as carbonyl and carboxylate functions (160-190 ppm).

Another sample of petroleum JP-5 was stressed with 0.0286 M DMP and 0.1 M thiophenol at 120° C, 10 days. The sediment obtained had the following analysis: C, 66.2; H, 6.1; O, 10.1; N, 7.9; S, 9.0. The formula is $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$. Figure 11 gives the solid-state C-13 spectrum of this sediment, which shows presence of appreciable methyl and aromatic or olefinic carbons (pyrrole), very small amount of carbonyl and carboxylate. In comparison with Figure 10, the DMP sediment (without sulfur) has a much greater content of carbonyl, carboxylate and methylene groups.

The Xps spectrum of the sediment, obtained by using both DMP and thiophenol as additives to petroleum JP-5 is shown in Figure 12. The C 1s, N 1s, and O 1s peaks are singlets whereas at least two sulfur species are involved. The existence of more than one sulfur species (probably some oxidation product) is confirmed by the S2p peaks in Figure 13.

The presence of both pyrrole and thiophenol fragments in the deposit would explain in part the synergistic effect in deposit formation and light scattering between the nitrogen and sulfur-containing compounds.

The XPS spectrum of a sediment obtained by stressing petroleum JP-5 with 0.0143 M DMP and 0.1 M thiophene, 50° C, 62 days, is very similar to Fig. 11, except that no sulfur peak is evident. An expanded spectrum in the S 2p region was also obtained and no peak appeared. These results are consistent with the data of Table 4, in that thiophene does not promote sediment formation. This is in sharp contrast with thophenol, which gives dramatic synergistic effect with DMP in sediment formation.

A low voltage high resolution mass spectrum of the above sediment was obtained. Table 6 contains a portion of the information. The probable compounds are listed in the order of decreasing peak intensity. Since thiophene is not incorporated, the compounds listed in Table 6 may be regarded as partial degradation products of DMP. Frankenfeld et al (5) have postulated possible partial structures for DMP sediment based on mass spectra at 70 eV. This high voltage produces fragments, so that a strict comparison with our low voltage (11 eV) data

is not possible. However, both results lead to the conclusion that the pyrrole ring is intact in the sediment. Frankenfeld et al (5) report that the sediments appear to be of fairly low molecular weight, little more than 400 mass units. Because of the low voltage used in our experiments, we have reported possible compounds (not fragments) in Table 6. We note that the sediment is indeed of low molecular weight, the highest being 216 mass units. From Table 6 we note also that a major oxidation product of DMP has the same structure as DMP except for a methyl group replaced by $-\text{CH}_2\text{OH}$. The OH group is not present in any of the possible structures for DMP sediment proposed by Frankenfeld et al. (5).

Our infrared spectra show OH absorption at 3360 cm^{-1} , the incorporation of oxygen in the sediment as carbonyl ($1640 - 1680\text{ cm}^{-1}$), as well as N-H, CH_2 and CH_3 absorptions. The infrared spectra thus support the probable structures reported in Table 6.

Conclusions

The results of this research confirm previous published findings that DMP is very deleterious to fuel stability. In addition to standard gravimetric procedures, we have applied light scattering and oxygen absorption techniques as monitors of fuel degradation. Laser light scattering measurements on particles forming and growing are particularly useful in observing degradation phenomena when heteroatomic compounds are added to a fuel. We have obtained the first direct evidence of the pyrrole radicals in DMP and NMP and shown that EPR spectroscopy is useful in characterizing the radicals. Of the sulfur compounds investigated, the aromatic thiol, thiophenol, is much more deleterious than decanethiol and other aliphatic sulfur compounds: dibutyl disulfide, dibutyl sulfide. The thiophenes (thiophene, tetrahydrothiophene) and unsaturated compounds (indene, 1-hexene, hexadienes) exert little deleterious effect. In the presence of DMP, positive synergism occurs between thiophenol and DMP leading to drastic enhancement in sediment formation and light scattering for jet fuel A, petroleum-JP-5 (No. 80-12) and petroleum diesel fuel. For petroleum JP-5 (80-8), the effect of DMP and thiophenol on sediment formation is additive. Synergism between the additives occurs most drastically with petroleum derived diesel fuel, which contains smaller amount of saturates and larger amounts of aromatics and sulfur than the jet fuels. Thus, the hydrocarbon composition and sulfur content influences stability.

We have applied nuclear magnetic resonance infrared, electron paramagnetic resonance, X-ray photoelectron spectroscopy and low voltage mass spectrometry techniques to characterization of deposits.

Sediments formed in the presence of DMP and thiophenol contain significant amounts of nitrogen and sulfur, whereas when thiophene replaces thiophenol, no sulfur is incorporated in the sediment. These results are consistent with sedimentation data in that thiophene does not promote sediment formation. This is in sharp contrast with thiophenol, which may give dramatic synergistic effect with DMP in sediment formation, particularly in diesel fuel.

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Table 1 Properties of liquid fuels

Specific gravity	Petroleum jet fuel LR29792	Petroleum JP-5 80-12	Petroleum diesel fuel LR30886
°API	42.1	39.5	34.5
Aniline point	144	-	144.5
Analysis of hydrocarbons, Vol. % FIA:			
Saturates	83.0	78.7	67.5
Olefins	1.8	1.3	1.0
Aromatics	15.2	20.0	31.5
Sulfur, ppm	125	300	2200

Table 2: Sedimentation results with DMP (0.0286 M in jet A LR 31613#3), g/100 mL fuel

After storage for	Insoluble sediment	Adherent sediment	Total sediment, W
2 days:			
43°	0.0008	0.0004	0.0012
67°	.0056	.0018	.0074
80°	.0172	.0035	.0207
4 days:			
43°	.0034	.0008	.0042
67°	.0165	.0038	.0203
80°	.0400	.0057	.0457
6 days*:			
43°	.0048	.0012	.0060
67°	.0312	.0047	.0359
80°	.0849	.0087	.0936
8 days:			
43°	.0043	.0031	.0074
67°	.0427	.0088	.0515
80°	.1206	.0132	.1338
10 days:			
43°	.0052	.0049	.0101
67°	.0532	.0078	.0610
80°	.1319	.0193	.1512
12 days:			
43°	.0116	.0043	.0159
67°	.0648	.0090	.0738
80°	.1358	.0090	.1448
12 days**			
43°	0.0005	0.0004	0.0009
67°	.0007	.0007	.0014
80°	.0011	.0007	.0018

*DMP concn. in jet A: 0.0294 M.

**no DMP added to jet A (blanks)

Table 3. Sediment^a from spiked jet fuel A LR 31613 #3

Compound added	Conc. in fuel, M	t _{1/2} , C	Time, days	Insol. Sed.	Adherent Sed.	Total W
Dibutyl sulfide	0.2	80	13	0.0002	0.0022	0.0024
Dibutyl disulfide	.2	80	13	.0000	.0044	.0044
Thiophene	.2	80	13	.0031	.0040	.0071
Tetrahydrothiophene	.2	80	13	.0033	.0025	.0058
Thiophenol	.1	43 67 80	4 4 4	.0005 .0004 .0005	.0013 .0064 .0095	.0018 .0068 .0100
Decanethiol	.1	43 67 80	32 32 32	.0014 .0016 .0025	.0011 .0026 .0031	.0025 .0042 .0056
NMP	.0286	43 67 80 43 67 80	32 32 32 42 42 42	.0006 .0008 .0007 .0003 .0012 .0018	.0007 .0005 .0010 .0010 .0009	.0006 .0010 .0012 .0013 .0022 .0027
Indene	.1	43 67 80	34 34 34	.0013 .0008 .0009	.0008 .0124 .0142	.0021 .0132 .0151
Indene	.2	80	12	.0017	.0028	.0045
1-Hexane +DMP	.2 .0286	43	12	.0051	.0109	.0160
1,5-Hexadine +DMP	.2 .0286	43	12	.0041	.0124	.0165
Thiophenol +DMP	.1 .0286	43 67 80	6 6 6	.0212 .0628 .1196	.0029 .0629 .0567	.0241 .1257 .1763

^a Sediments in g/100 mL fuel were mean of duplicate determinations; duplicate weights agreed to within 10%.

Table 4. Results of duplicate determination of sediment formation (insoluble & adherent) when liquid fuels are subjected to accelerated ageing in the presence of additives at 50° C^a

N-compound ppm (N)	S-compd	Sediment (mean, total, mg/100 mL)			
		Petroleum jet fuel (LR 29792) 7 days	Petroleum JP-5 (80-8) 20 days	Petroleum JP-5 (80-12) 20 days	Petroleum diesel LR 30886 7 days 13 days
0	0	0.6 (0)	0 (0)	0 (0)	0 (0) 1.2 (0.1)
0	0.1M PhSH	3.4 (0.4)	6.1	24.0 (0.2)	7.6 (0.9) 16 ^b
0	0.1M THT	0.4 (0.2)			
0	0.1M thiophene	0 (0)			
200, DMP	0	4.4 (0)	16.5	25.4 (2.5)	18.2 (2.3)
200, DMP	0.1M PhSH	47.1 (1.8)	22.3 (1.1)	85.6 (0.6)	106.5 (12.5)
200, DMP	0.1M THT	3.5 (0.6)			
200, DMP	0.1 M thiophene	3.2 (0.2)			
500, DMQ	0	0 (0)			2.7 (0.4)
500, DMQ	0.1M PhSH	40.1 (3.2)			21.6 (0.8)
500 DMQ	0.1 M thiophene	0.2 (0.1)			
500 DMQ	0.1 M THT	0 (0)			






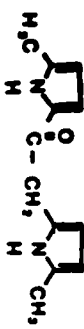
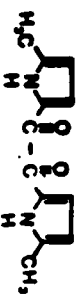
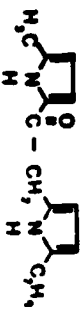

^aSediment values are corrected for blank. Values in parenthesis are average deviations. PhSH=thiophenol, THT=tetrahydrothio-
phene, DMQ=2,6-dimethylquinoline.

^bestimated

Table 5. Sedimentation formation with 2,6-Dimethylquinoline (DMQ) and/or other additive after storage in test fuel at 50 °C for fourteen days.

FUEL	ADDITIVES		SEDIMENT (mg/100 mL)		TOTAL
	DMQ	OTHER (N)	INSOLUBLE	ADHERENT	
Petr. Jet (ppm) (0. 1M)					
LR-31284	0	0	0.4	0.0	0.4
	500	0	0.0	0.0	0.0
	0	Butyldisulfide	0.0	1.1	1.1
	500	Butyldisulfide	0.0	1.6	1.6
	0	n-Butylsulfide	0.2	0.0	0.2
	500	n-Butylsulfide	0.0	0.0	0.0
	0	THT	0.0	0.0	0.0
	500	THT	0.0	0.1	0.1
	0	Thiophenol	0.8	8.0	8.8
	500	Thiophenol	50.4	1.8	52.2
	0	1-Hexene	0.0	0.4	0.4
	500	1-Hexene	0.2	1.5	1.7
	0	1,5-Hexadiene	0.0	1.6	1.6
	500	1,5-Hexadiene	0.0	1.0	1.0

Table 6. Some identified peaks for the low voltage high resolution mass spectrum for the sediment obtained by stressing petroleum jet fuel with 0.014 M DMP and 0.1 M thiophene, 323 K, 62 days

Probable Structure	Molecular Formula	Measured Mass	Calculated Mass	δ Int.
	C_6H_9NO	111.0719	111.0682	100.00
	C_5H_7NO	97.0533	97.0526	81.85
	C_6H_7NO	109.0563	109.0526	60.83
	$C_{11}H_{12}N_2O$	188.0955	188.0947	51.27
	C_7H_9NO	123.0703	123.0682	25.75
	$C_{12}H_{14}N_2O$	202.1078	202.1103	15.26
	$C_{12}H_{12}N_2O_2$	216.0900	216.0896	11.12
	$C_{13}H_{16}N_2O$	216.1265	216.1259	7.83
	$C_{11}H_{10}N_2O_2$	202.0766	202.0740	4.24

Legends of Figures

- Fig. 1 Laser light-scattering at scattering angle 90° , I_{90} , as function of storage time at room temperature of petroleum JP-5, upgraded H-coal liquid (LHSV 0.5) and shale JP-5, in the absence and presence of 2,5-dimethylpyrrole (DMP).
- Fig. 2 Plots of total sediment weight (W) vs. time at 43, 67, 80° C for sediments formed from 200mL jet fuel A (LR31613#3), 0.0286M DMP.
- Fig. 3 Plots of $\ln W$ vs $1/T$ for system of Fig. 2
- Fig. 4 Plot of I_{90} vs. time for petroleum JP-5 (80-12), 50 ppm (N) DMP and additives.
- Fig. 5 Light scattering curves of 0.2M indene and 0.2M decanethiol in jet fuel A at 25° and 80° C.
- Fig. 6 Light scattering curves for 0.2M dibutyl sulfide and dibutyl disulfide in jet fuel A at 25° and 67° C
- Fig. 7 Oxygen absorption curves for pure DMP and NMP
- Fig. 8 Oxygen absorption curves for pure 2,4-hexadiene and 1-hexene
- Fig. 9 EPR spectrum of deposit from stressing jet fuel A with 0.0286M DMP, 80° C, 6 days
- Fig. 10 Top: solid-state C-13 NMR spectrum of insoluble sediment from petroleum JP-5, 0.0286M DMP, 120° C, 10 days
Bottom: spectrum of the same sediment in a dipolar dephasing sequence in which 40 μ sec post delay has been inserted.
- Fig. 11 Magic-angle solid-state C-13 spectrum of sediment obtained by stressing petroleum JP-5 with 0.0286M DMP and 0.1M thiophenol, 120° C, 10 days
- Fig. 12 XPS spectrum of the sediment of Fig. 11
- Fig. 13 XPS S2p peaks of Fig. 12

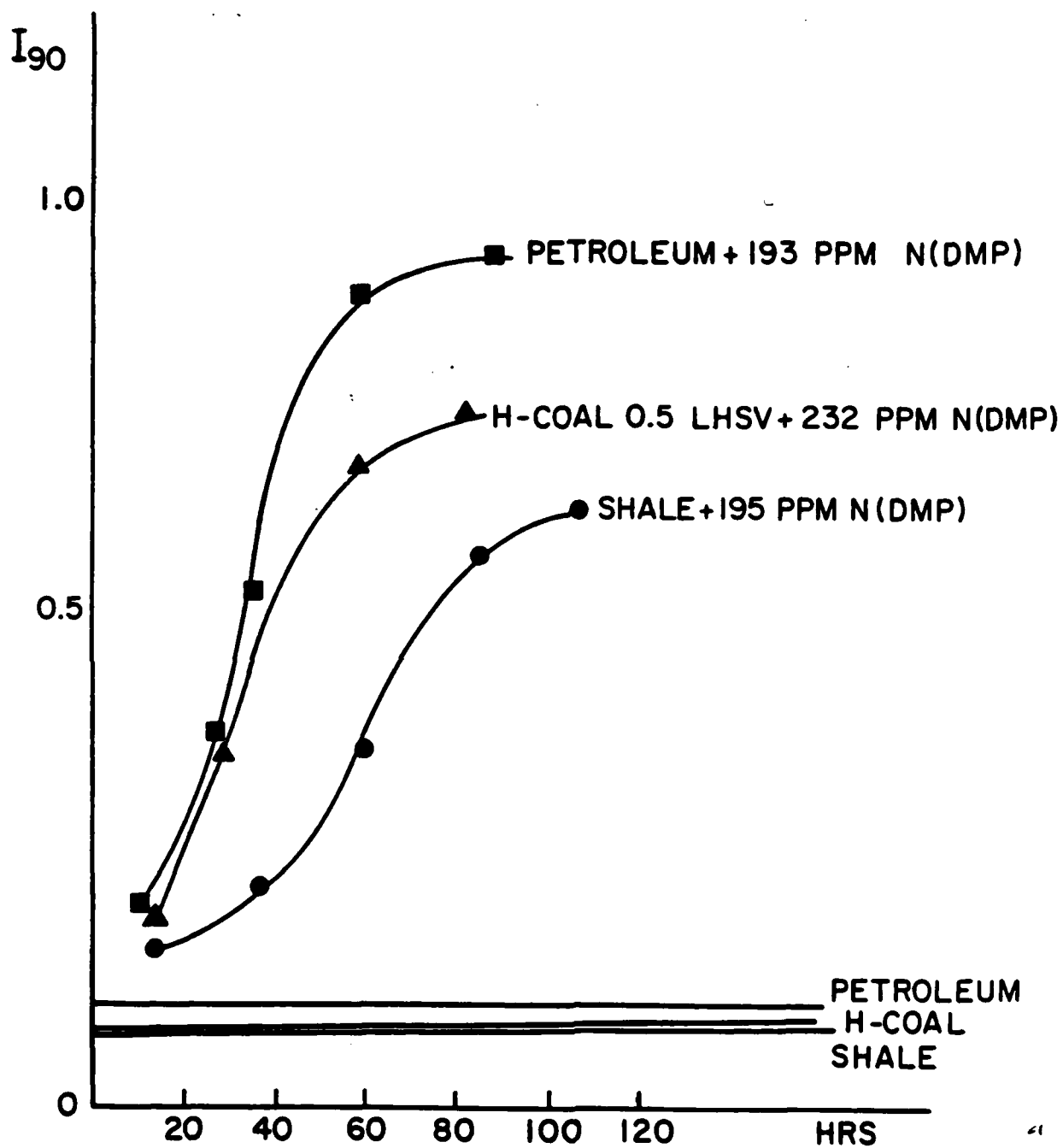


Fig. 1

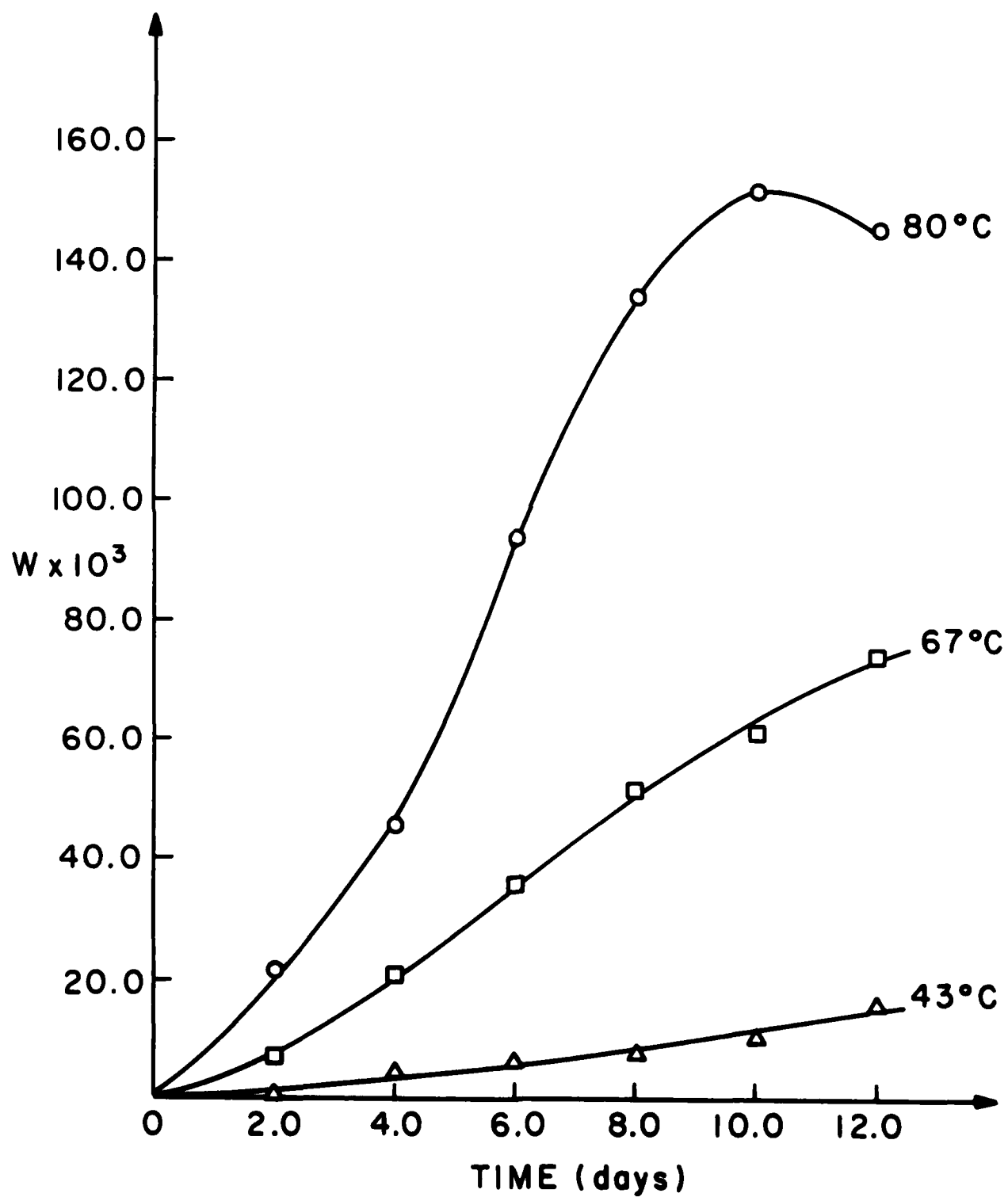


Fig. 2

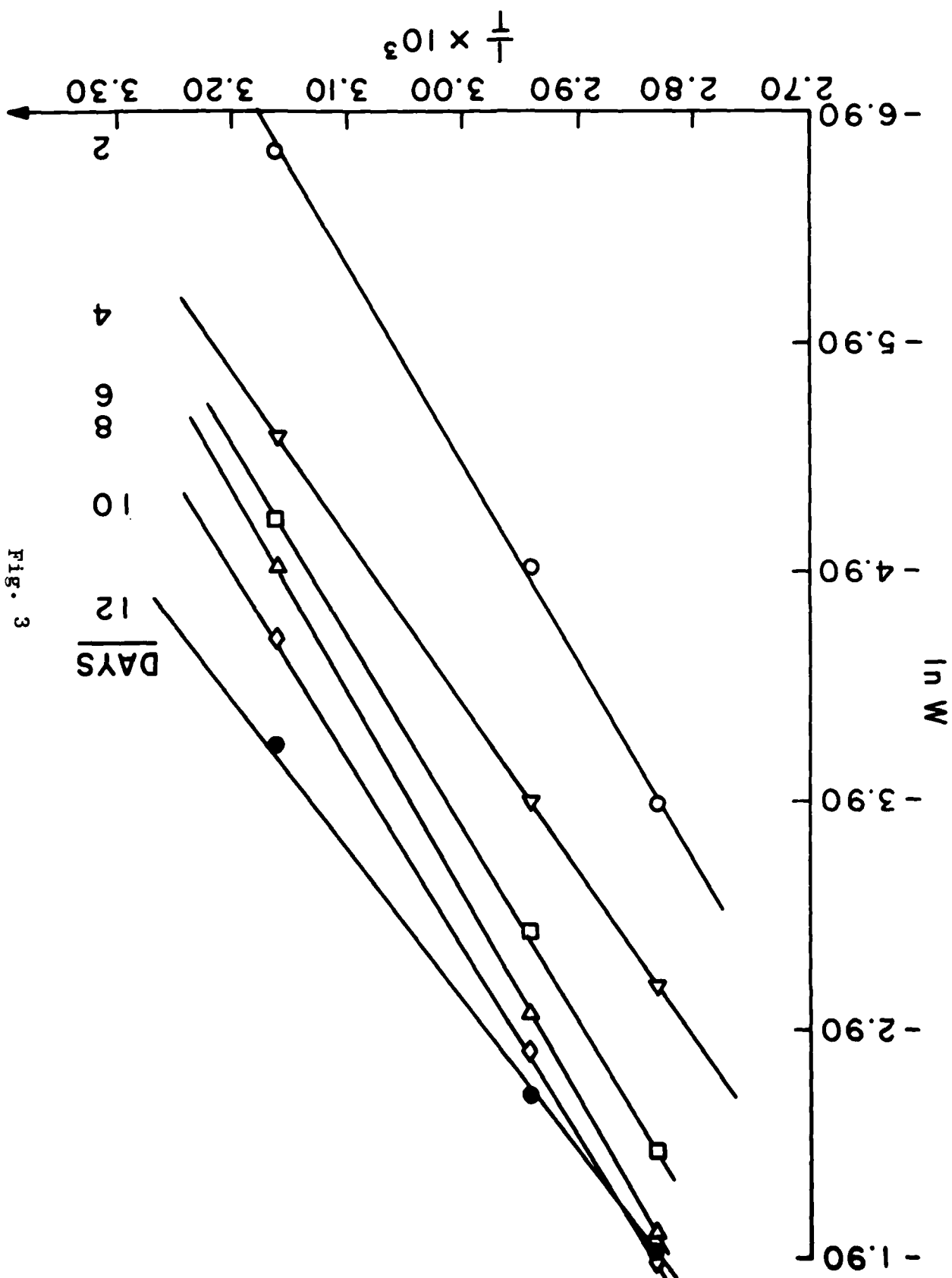


Fig. 3

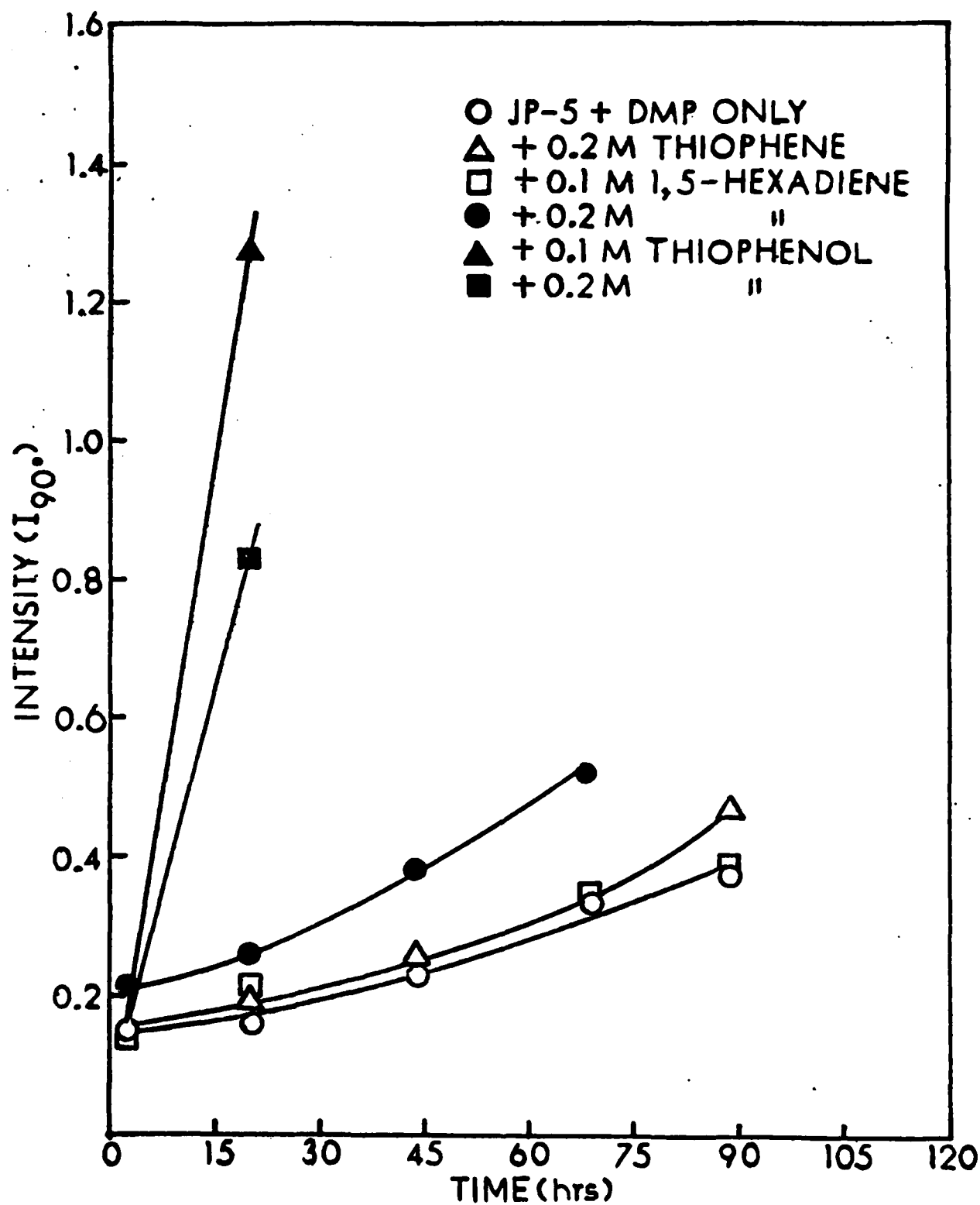
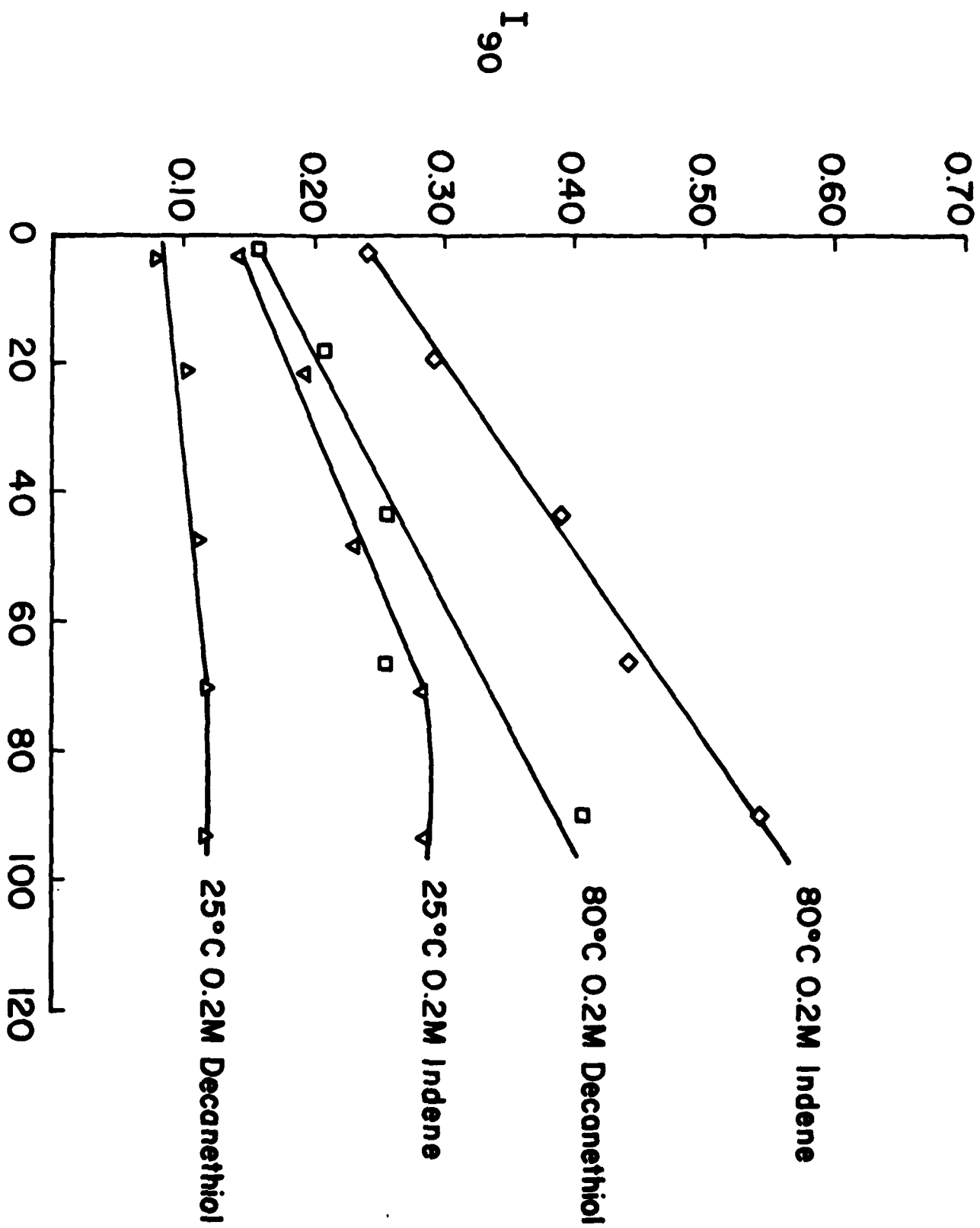


Fig. 4



Time (hrs)
Fig. 5

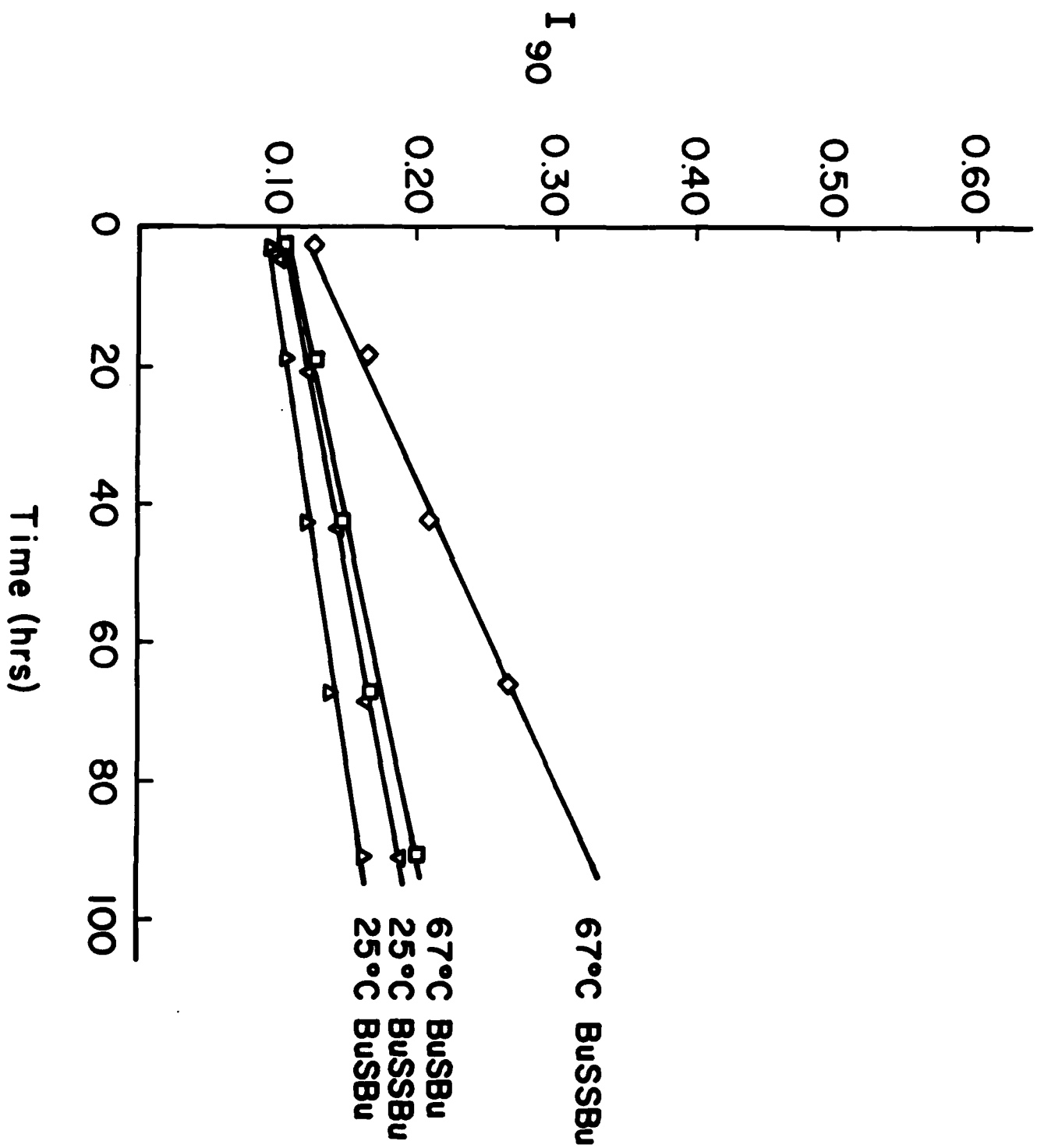


Fig. 6

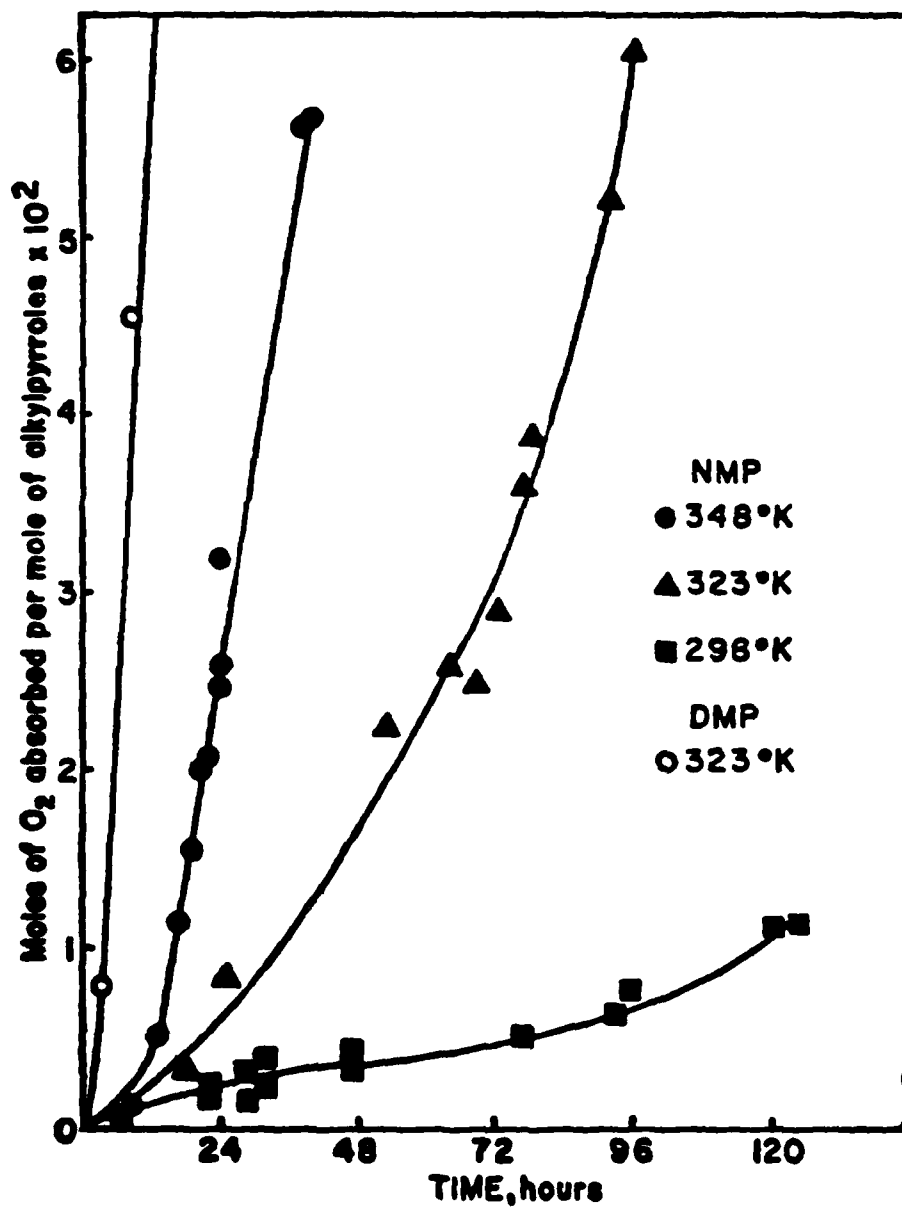


Fig. 7

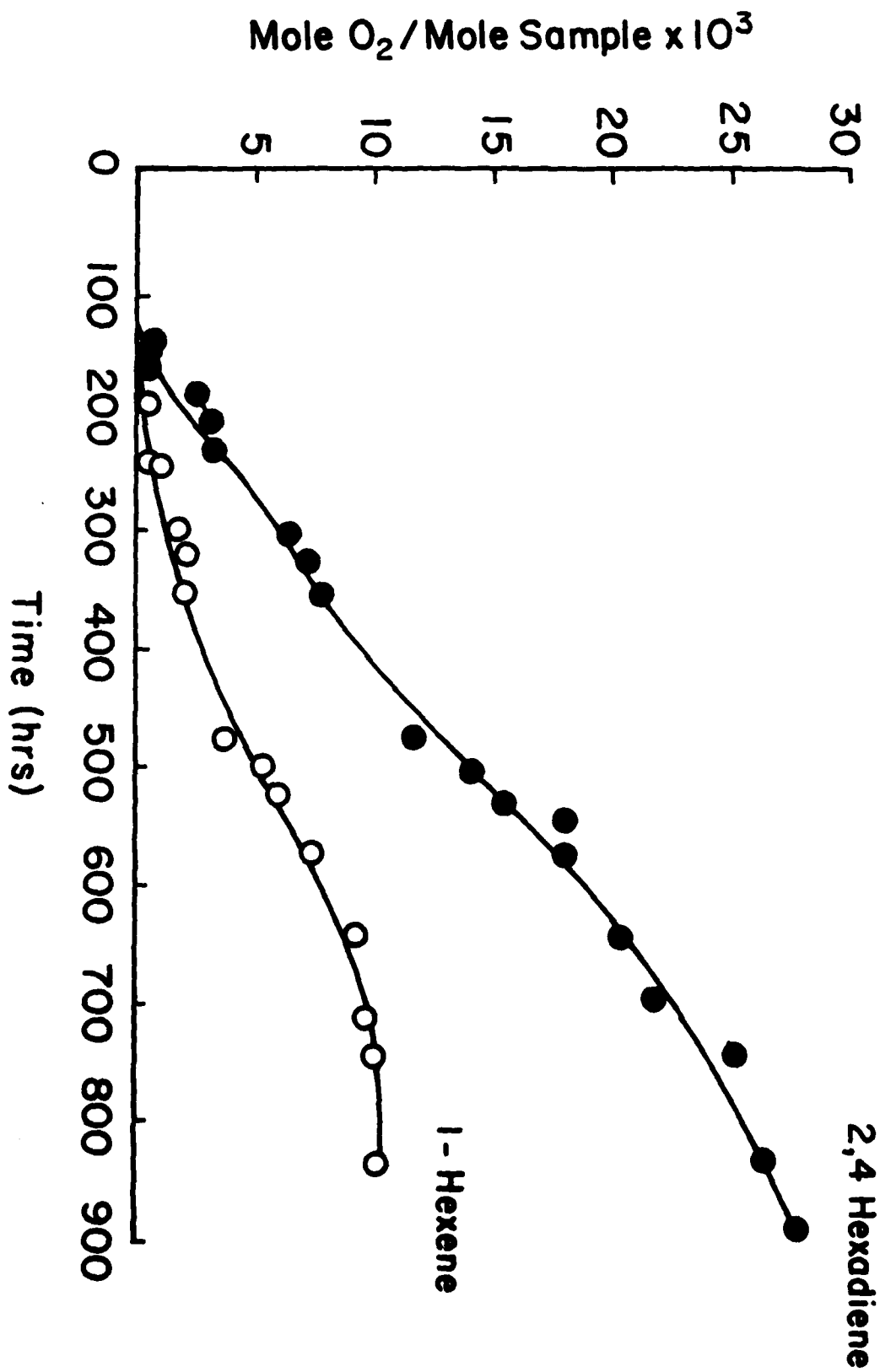


Fig. 8

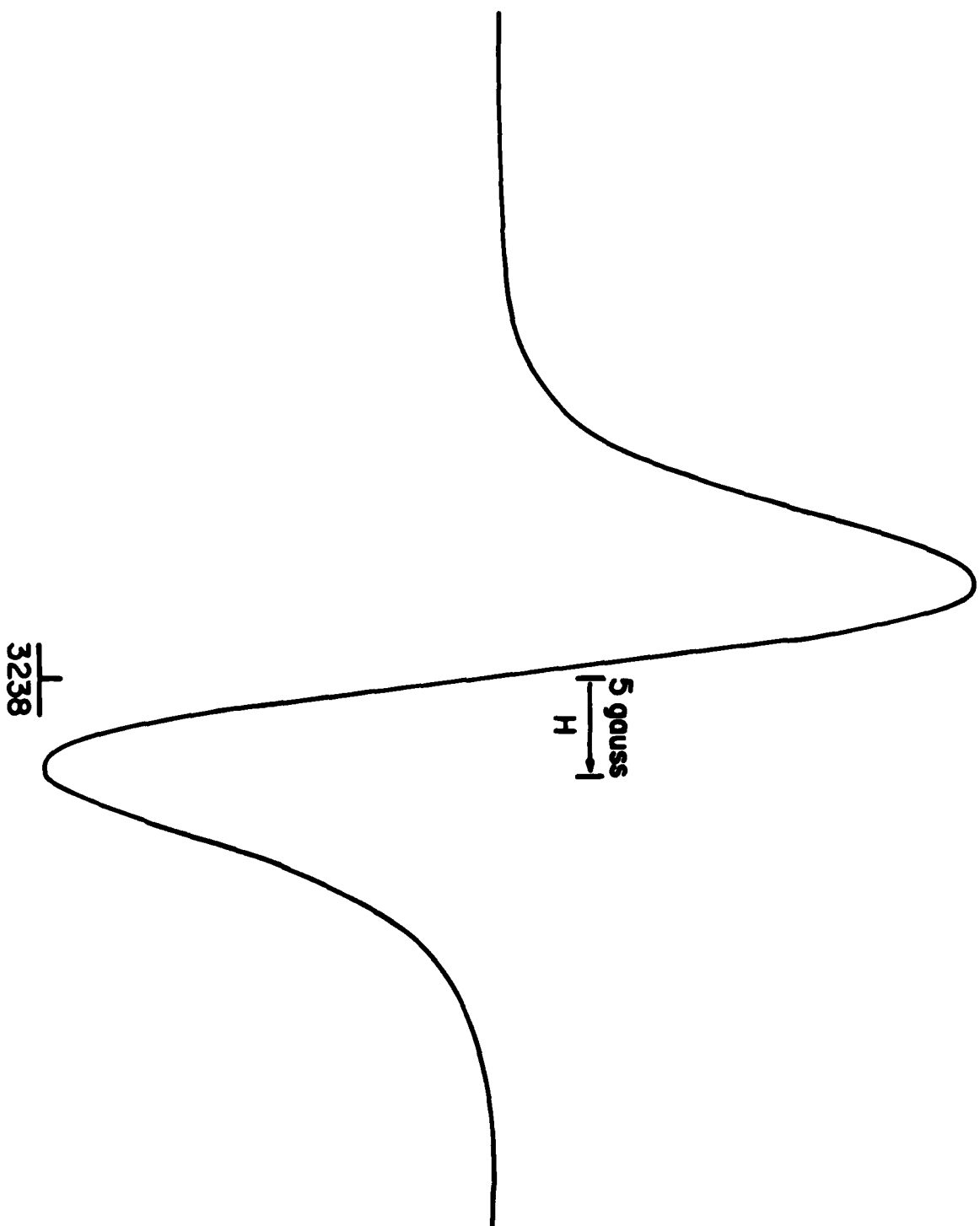


Fig. 9

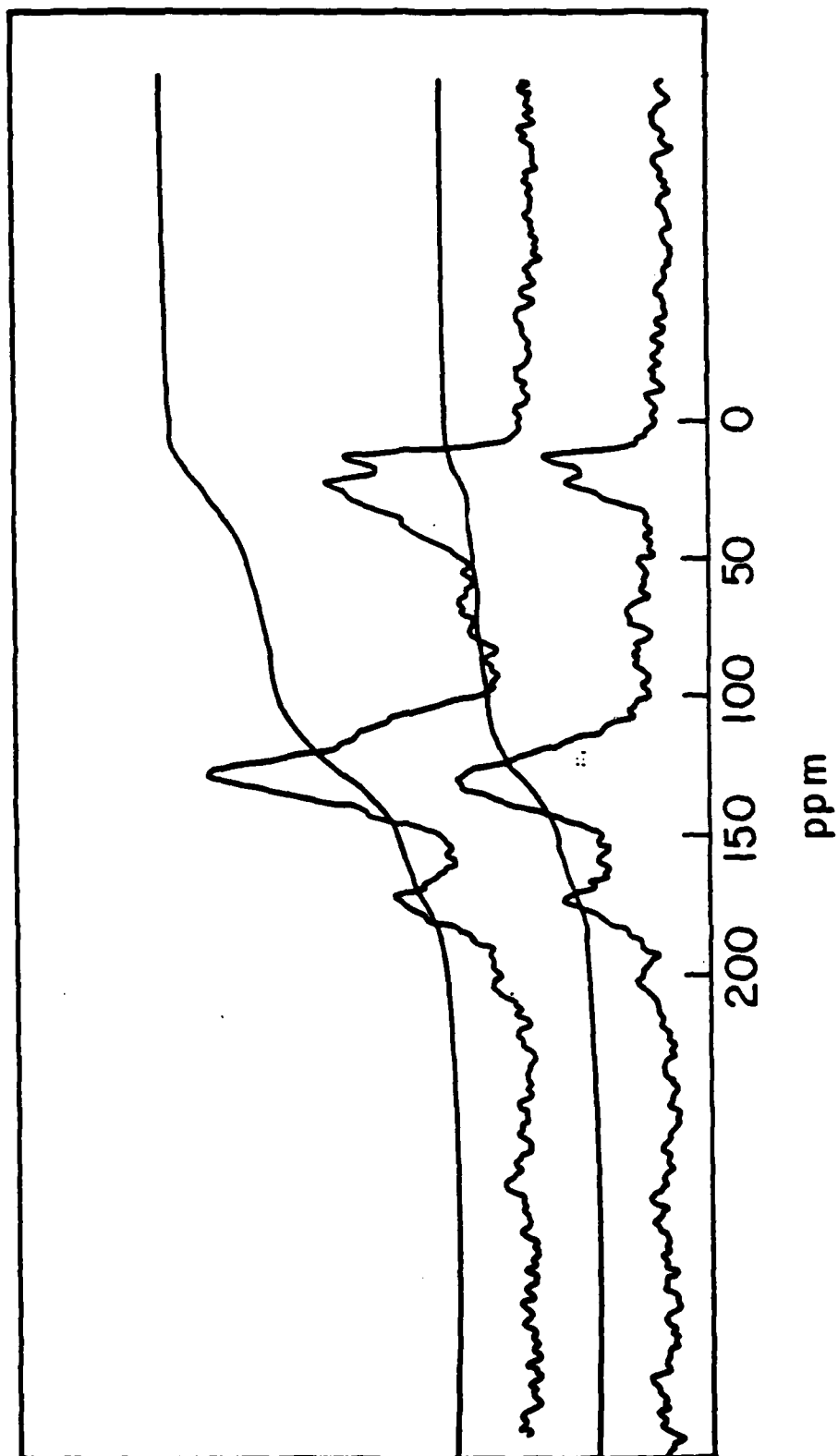


Fig. 10

JP-5 (DMP, C_6H_5SH)

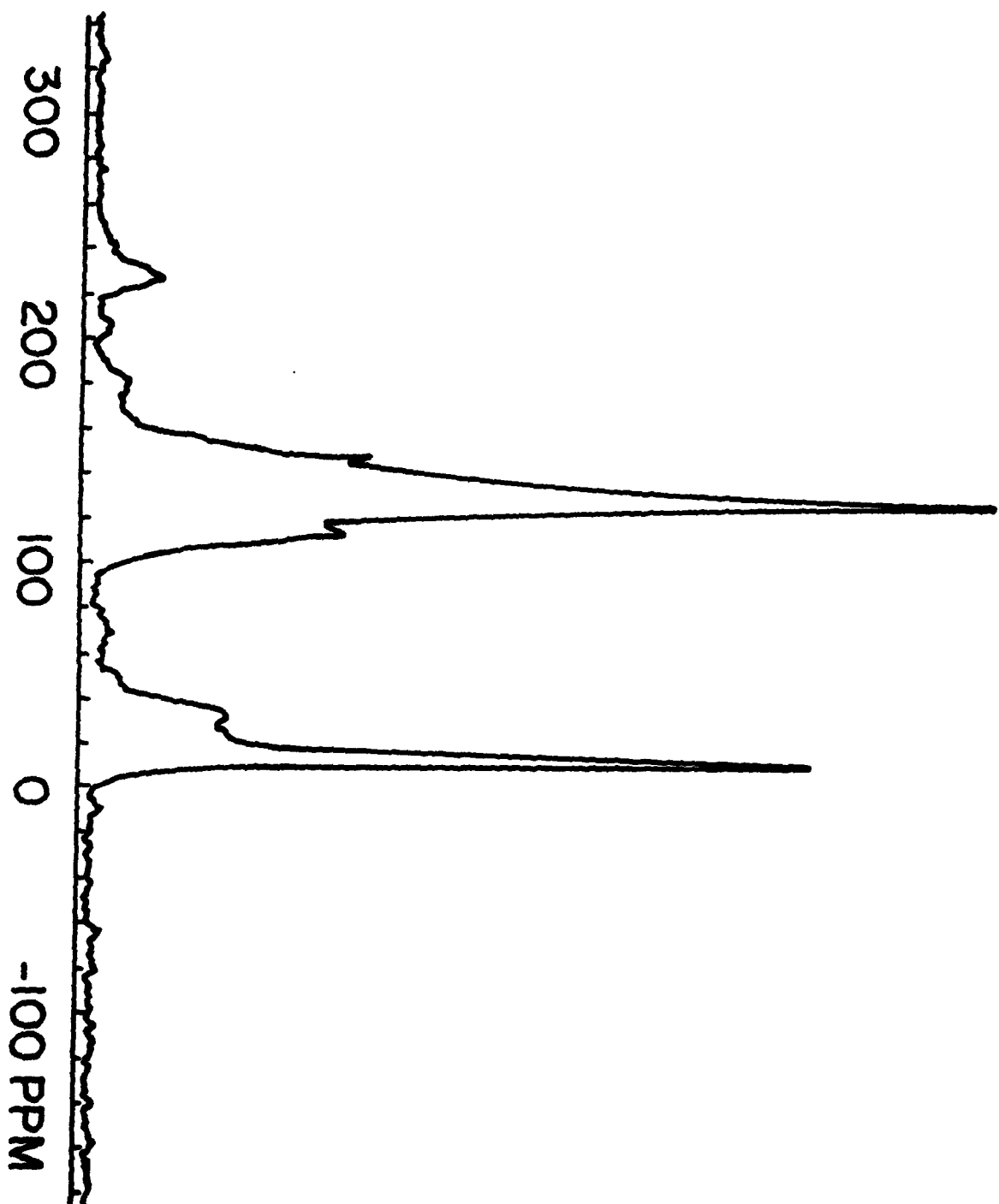


Fig. 11

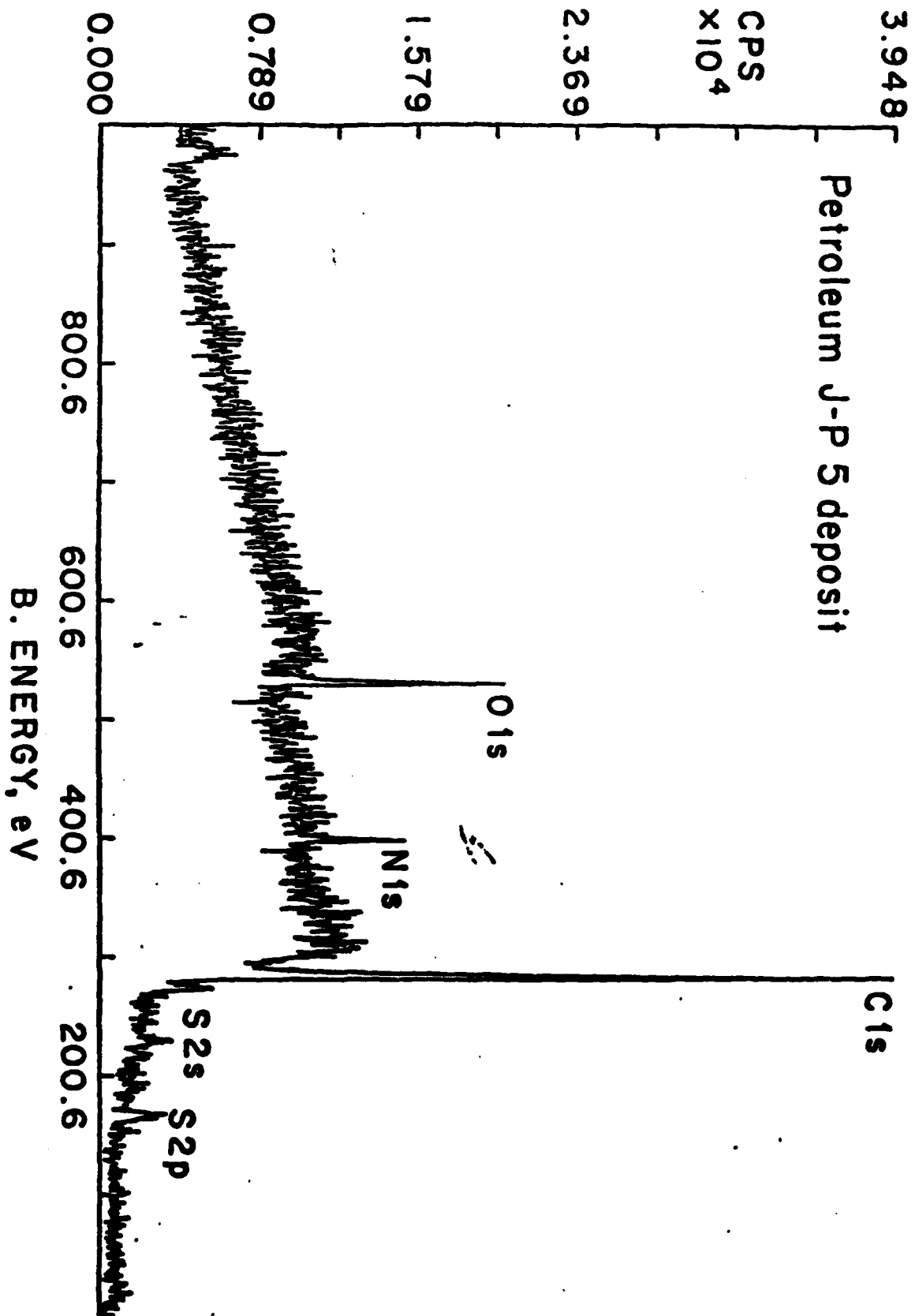
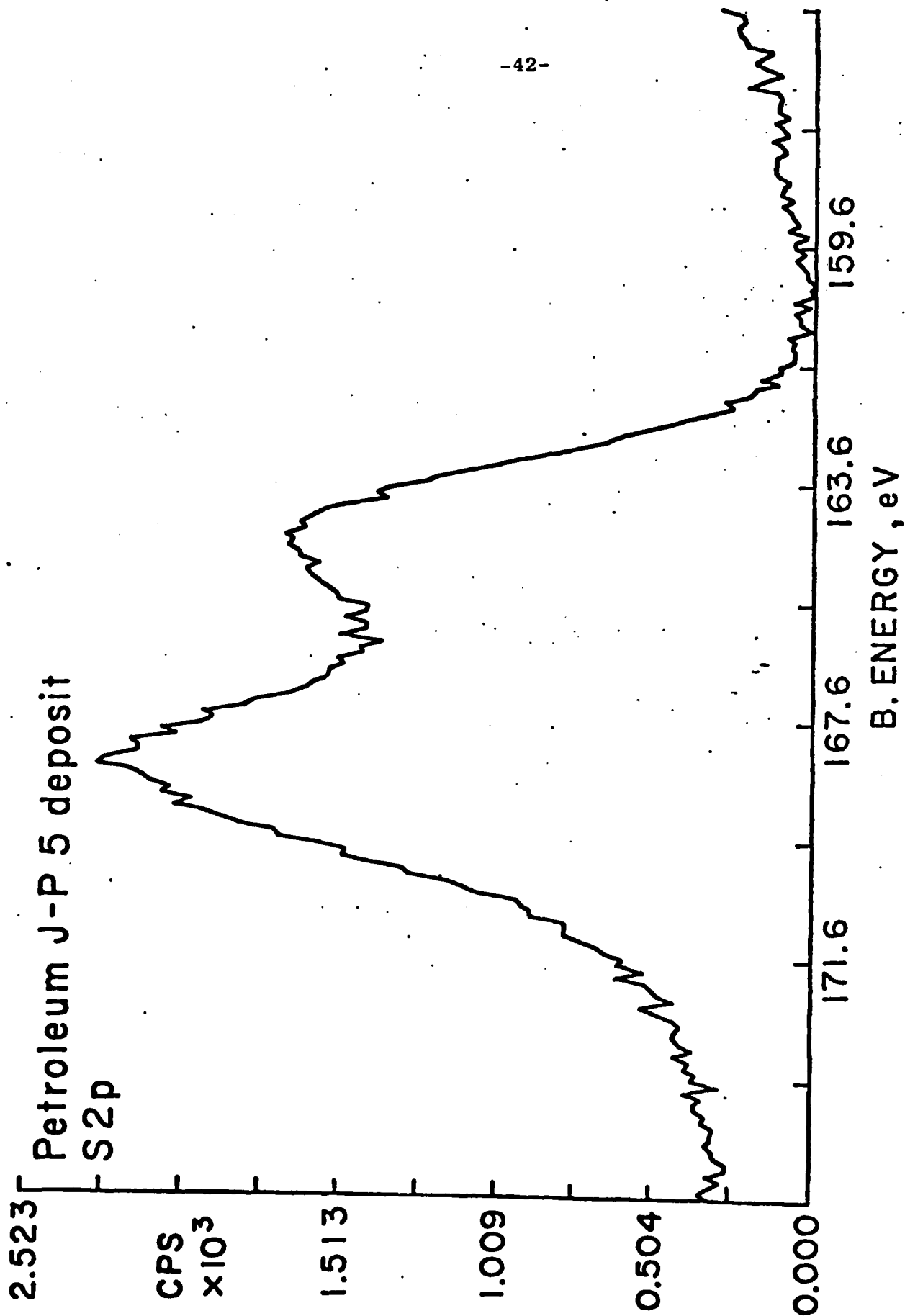


Fig. 12



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